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Heavy Metals—an Inventory of Existing Conditions[1]

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ABSTRACT

In this paper we report on studies undertaken to: (1) establish mercury levels in biota and sediments from the lower portion of Chesapeake Bay; (2) describe the pattern of metal distribution in oysters from 3 Virginia estuaries; and (3) determine if estuarine sediments can be used to detect the effects of man's activities on the environment. To date, mercury analyses of biota from the Bay area have shown no levels in excess of FDA guidelines, nor have they indicated any influence of man's activities in the areas studies. Oysters have been shown to vary naturally in their body burdens of the heavy metals—copper, cadmium, and zinc—and techniques are suggested whereby unnatural heavy metal inputs can be identified. Sediments from an industrialized river system have been shown to reflect the inputs from human activities.

An attempt is made in this report to inventory the status of knowledge on certain metallic elements in the lower portion of Chesapeake Bay. Some of the data presented have been published or submitted for publication elsewhere, and in all cases the sources of information are identified. Much can be learned from what we have called the inventory approach, as one in an attempt to explain what has been observed is usually forced to consider many variables which *a priori* were not thought to be significant. During this process, interpretations are frequently made which suggest avenues for future research. Initially, however, the objective of any inventory is to establish the existing conditions—in this case, the distribution of certain heavy metals in sediments and biota from the Bay region. Studies of the

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[2]Dr. Bender received his B.S., M.S., and Ph.D. degrees in zoology, fisheries, and environmental sciences, respectively. He is a member of 9 professional societies, is currently the principal investigator or co-investigator of 6 research grants, and has co-authored 13 scientific papers. He is the Assistant Director, Virginia Institute of Marine Science.

inventory nature are generally begun for a variety of reasons. Among these are:

1. Do the residue levels in certain commercial species exceed health standards or guidelines?
2. How is the distribution of certain elements influenced by natural phenomena?
3. Can one discern the influences of man upon natural systems?

In this paper we report on studies undertaken to: 1) establish mercury levels in biota and sediments from the lower portion of Chesapeake Bay; 2) describe the pattern of metal distribution in oysters from 3 Virginia estuaries; and 3) determine if estuarine sediments can be used to detect the effects of man's activities on the environment.

Mercury in Sediments and Biota

All analyses for mercury were conducted by flameless atomic absorption spectrophotometry. Sediment samples from the James, York, and Rappahannock were collected during the fall of 1970 from the channel at each station with a Petersen grab. Three grabs were taken from each location and the upper 3 cm of sediment from each was removed for individual analysis. Dried samples were screened through a 63-micron sieve, and only that portion of sediment passing through the screen was retained for analysis. The core sample was obtained from the Rappahannock River and subsamples from it were not screened. Approximate age of the oldest, i.e. lowest, portion of the core is 300 years (Nichols, personal communication). Digestion of the sediment samples was accomplished by oxidizing a 0.25-g sample with 5 ml of concentrated H_2SO_4 and 7.5 ml of a 6% aqueous potassium permanganate solution.

Mercury determinations in animal tissues were conducted on edible muscle only, with the exception of oysters which were completely digested. Duplicate samples from fish and crustacenas were taken. Collections were made during the fall of 1970 and the spring and summer of 1971.

Results obtained from the survey of 3 Virginia rivers are shown in Fig. 1. Statistical analyses showed no differences (5% signifi-

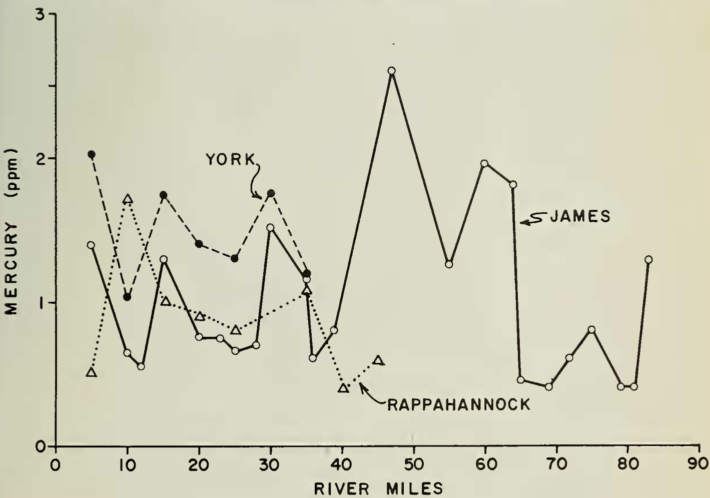

Fig. 1.—Distribution of mercury in sediments from three Virginia rivers.

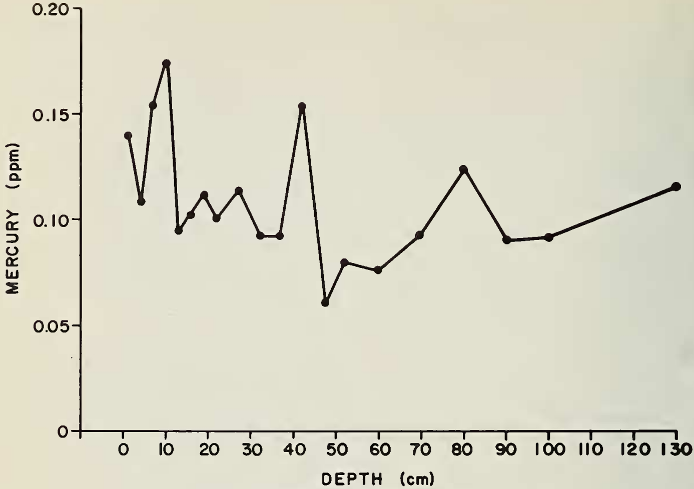

Fig. 2.—Mercury vs. depth in a core sample from Rappahannock.

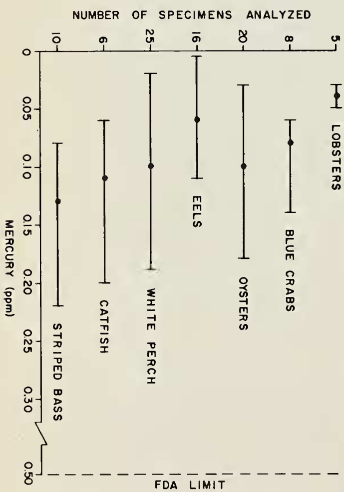

Fig. 3.—Mercury levels in selected animals.

cance level) within rivers with respect to distance from the mouth, or between rivers (Huggett *et al.*, 1971a).

Mercury concentrations found in the core sample as a function of depth are shown in Fig. 2. No indication of man's influence is evident from this core sample, as has been recently shown by Kennedy *et al.* (1971) from sediment cores taken in Lake Michigan.

Fig. 3 shows the mean and range of mercury levels found in various specimens collected from the Bay and Continental Shelf regions. Lowest levels were found in lobsters collected from Norfolk Canyon, while the highest were found in striped bass collected in the York River. The highest mean value, i.e. for striped bass, of 0.13 μg/g was well below the FDA limit of 0.50 μg/g.

Patterns of Metal Distribution in Oysters

The study described in this section is based on an investigation conducted during a period from February to May 1971 in which a total of 495 oysters were collected from

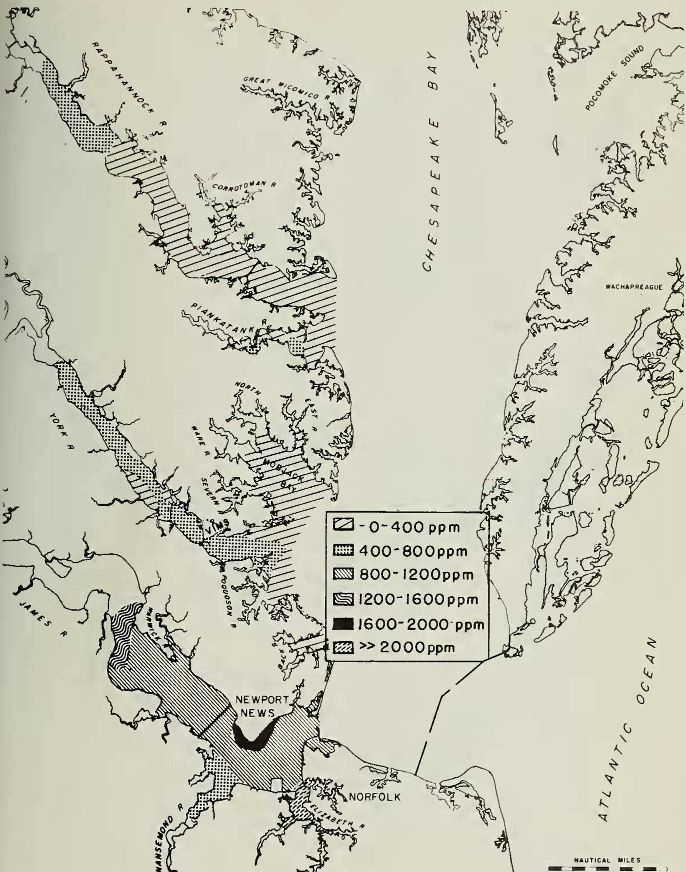

Fig. 4.–The distribution of zinc in oysters from Virginia's major rivers (from Proceedings of 7th National Shellfish Sanitation Conference).

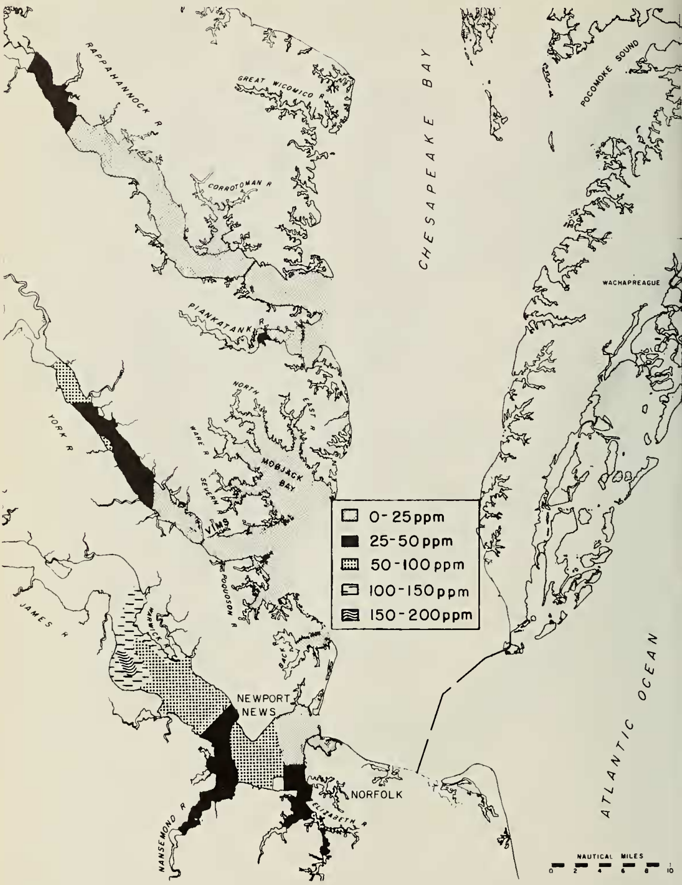

Fig. 5.–The distribution of copper in oysters from Virginia's major rivers (from Proceedings of 7th National Shellfish Sanitation Conference).

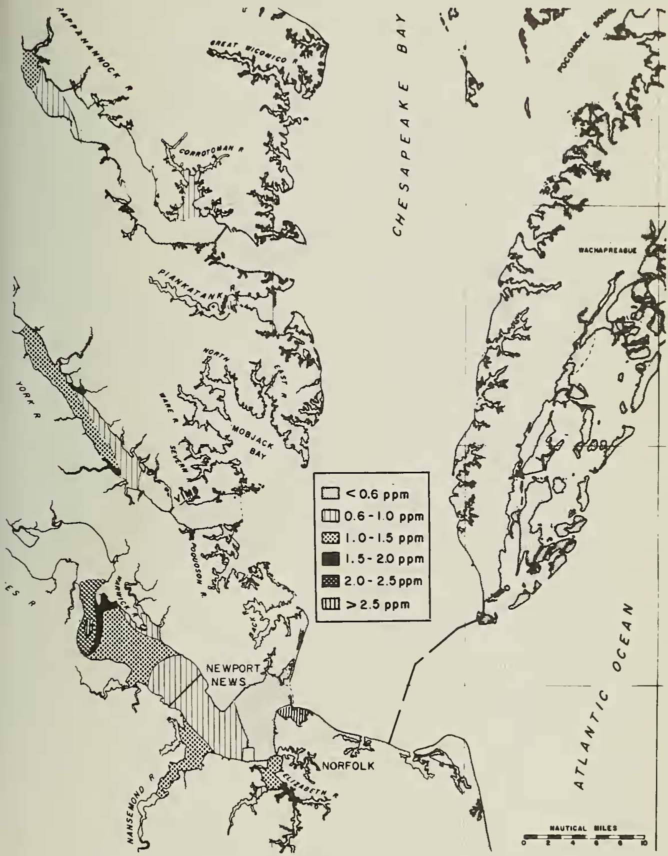

Fig. 6.–The distribution of cadmium in oysters from Virginia's major rivers (from Proceedings of 7th National Shellfish Sanitation Conference).

99 stations in the lower Bay (Huggett *et al.*, 1971b). Salinities at these stations ranged from 32‰ for the ocean side Eastern Shore to 7‰ in the upper reaches of the rivers. Five specimens from each site ranging in weight from 2 to 35 g were digested in concentrated nitric acid. The dissolved samples were analyzed for cadium, copper and zinc by atomic absorption.

Examination of the data showed that although oysters from the same location often varied in concentration by 100‰, there was no relationship between age of the oyster as indicated by weight and the metal concentration.

Average metal concentrations were used in this study only to establish the areal distribution of metals in the various river systems. The means showed that a concentration gradient existed in all systems, and that each metal increased in concentration as fresh water was approached (Figs. 4, 5, 6).

To account for these observations, the following assumptions are proposed:

1) The metals (Cd, Cu, and Zn) available to oysters in non-industrialized areas are from the natural weathering of rocks.

2) The ratio of copper to zinc in the weathering rocks is relatively constant within a drainage basin.

3) Oysters accumulate a constant percentage of each element available to them.

4) Some factor, e.g. salinity or humic acid concentration, varies predictively with distance, causing the amount of metal available for uptake to vary.

If these assumptions are valid, one should be able to establish a relationship between various metals in oysters taken from areas which have similar drainage basins. Furthermore, if such relationships for naturally occurring phenomena can be established, perhaps a method can be developed to identify unnatural inputs.

To establish whether there was a relationship between one metal and another, the zinc and copper concentrations from all samples taken from rivers which extend above the fall line and in which there is no known unnatural zinc or copper source are plotted in Fig. 7.

The placement of confidence bands around this line, which is intended to represent background conditions, would allow for a simple and direct method to detect outliers or "unnatural" inputs. However, the use of normal confidence intervals requires that there be an independent and a dependent variable. If the assumptions previously outlined are correct, then both variables are independent, i.e., the zinc concentration does not control the copper concentration. Hence, the authors have placed a band, consisting of 2 straight lines, around the least squares line. The band encompasses 95% of the points and can be thought of as an approximate confidence band. The equations for the 2 lines are:

$$Y = -33 + 0.07X$$
$$Y = -30 + 0.11X$$

Oysters collected from areas of suspected unnatural inputs, as well as those falling outside the limits established from Fig. 7, are plotted along with the confidence band in Fig. 8. It appears that the Elizabeth River and Hampton Roads, both highly industrialized, are contaminating the oysters in their immediate areas as well as the lower reaches of the James River with zinc. In the upper James, an unnatural source of copper is indicated by points falling on the copper side of the band in Fig. 8.

Metal Sediment Relationships

In the late summer of 1971 a survey of the pollutants present in sediments of the James River system was initiated. The objective of the study was primarily to establish whether the existing levels of certain materials in these sediments would prohibit the disposal of dredgings into open waters, as based on guidelines established by the Environmental Protection Agency. The results reported here were obtained from the Southern Branch of the Elizabeth River, where at present all spoil materials from dredging operations are disposed of in a specially constructed site (Craney Island). Three samples collected across the channel were obtained at 0.25-mi intervals with a 3-ft gravity corer. Sediment from each core was completely

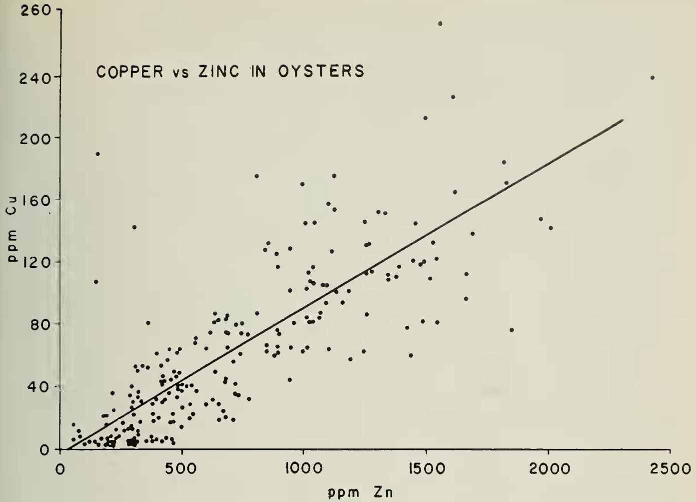

Fig. 7.—Relationship between zinc and copper in oysters from Virginia's major rivers (from Proceedings of the 7th National Shellfish Sanitation Conference).

homogenized before subsamples were taken for analysis.

Concentrations of the metals copper, lead, mercury, and zinc found in Elizabeth River sediments are shown in Fig. 9. Several significant observations can be made from this figure: 1) there appears to be an input of all metals at miles 9.5 and 8.5; 2) an input of just zinc at about mile 7; and 3) inputs of both zinc and copper at mile 5. From these data it is apparent that the levels of metals in these sediments reflect inputs from man's activities and that the sediment levels are sufficiently distinct to allow for the recognition of specific metal inputs.

Discussion

Mercury levels reported for sediments from 3 Virginia rivers—the James, York and Rappahannock—did not show evidence of man's influence. However, sediments from the Southern Branch of the Elizabeth River, a much smaller river, did indicate inputs from man. The only other analyses for mercury in sediments from the Bay have been reported by Pheiffer (1972) for the Potomac—the levels found there were extremely low, highest value reported 26.20 ppb, compared with our results.

The concentration banding of heavy metals by oysters has been shown to follow a predictable pattern and allows for the use of the oyster to identify unnatural metal inputs. The cause of this banding pehnomenon is, however, unknown. Drobeck and Carpenter (1970) reported variations in metal uptake with salinity and attempted to discern the role of sediments in the uptake of metals by the oyster. They concluded that metal uptake was highest in low salinities and was not related to natural sediment loads. A recent laboratory study completed by Lunz (1972) confirmed their results, demonstrating that dissolved copper was taken up much more readily than copper adsorbed to clay particles. The authors believe that the form of the metal in solution is responsible for the banding phenomenon and that the inter-

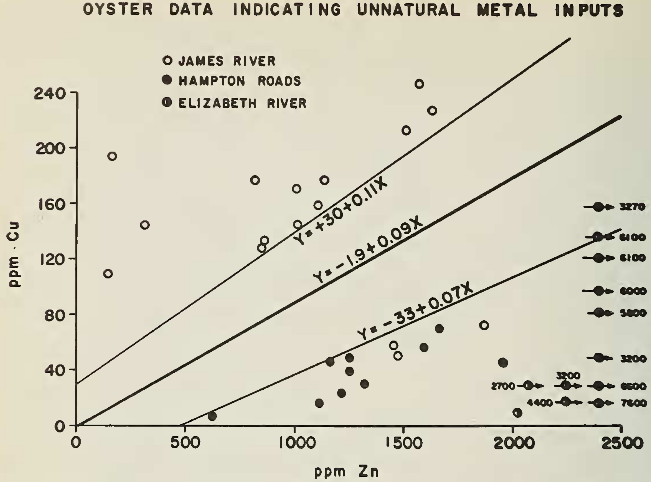

Fig. 8.–Oyster data indicating unnatural metal inputs (from Proceedings of 7th National Shellfish Sanitation Conference).

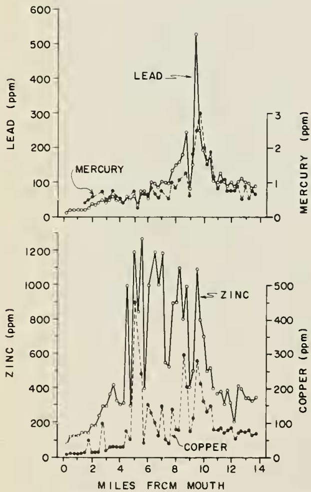

Fig. 9.–Metals in sediments from the Southern Branch of the Elizabeth River.

action of the sediments, which serve as sumps for metals, with the overlying waters, plays an important role in the overall process.

A study is underway to determine whether metal concentration ratios, determined on certain size fractions of sediments, can be used to detect unnatural metal inputs. This study is an extension of our oyster work and if successful should allow investigators to survey entire river systems, where oysters limit the investigators to particular salinity regimes.

Sediments from the Southern Branch of the Elizabeth have been shown to reflect inputs from man's activities. Similar results have been reported by Pheiffer (1972) in a study of the Potomac, where sediment analysis showed increases of lead, cobalt, chromium, cadmium, copper, nickel, zinc, silver, barium, aluminum, iron, and lithium in a critical area of the upper estuary. Inputs were attributed to both wastewater treatment facilities in the upper river and steam generating electric plants further downstream.

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Trace Element Analysis by Proton-Induced X-ray Excitation

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ABSTRACT

A new technique for detecting trace elements by exciting characteristic X-rays through proton bombardment is described. Typical results from analyses of algae, perch blood serum, perch liver, and sediment samples are presented.

Today I want to bring to your attention a new technique for trace element analysis that should be useful in evaluating many pollution problems of the Chesapeake Bay. The technique involves the excitation of atomic X-rays by bombardment with energetic protons. The X-ray production probabilities for such bombardments are sufficiently large that only small sample size is required. For example, one drop of blood is sufficient to detect trace elements in blood.

The technique is described schematically in Fig. 1. A beam of protons from the University of Maryland 3 MV Van de Graaff accelerator is incident upon a target sample. The incident protons pass through the thin target and lose a small fraction of their energy in the target by interaction with electrons in the target. Some protons remove electrons from the K-shell of atoms in the target with subsequent characteristic X-ray emission. The X-rays leave the target and pass through a 1-mil Be window on the target chamber and into a Si(Li) X-ray detector. It is the development of this high resolution detector that makes this technique so feasible and attractive. An X-ray from the target is completely absorbed in the active volume of the detector, producing an electronic signal of amplitude proportional to the incident X-ray energy. These signals are amplified and stored in a multichannel pulse-height analyzer. A measurement of the energy of the characteristic X-ray identifies the element in the target from which the X-ray originated. Knowledge of the number

[1]The author is an experimental nuclear physicist by training and has carried out numerous investigations into the structure of the light nuclei using nuclear reactions induced by ions from Van de Graaff accelerators. His recent interests have extended to using positive ions in studies of radiation effects, atomic physics, and trace element detection.